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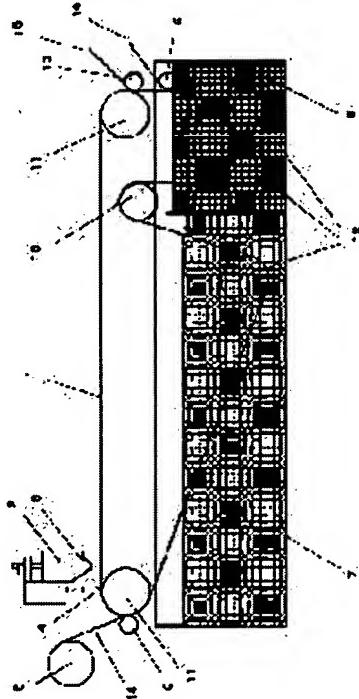
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(54) METHOD AND APPARATUS FOR CONTINUOUSLY MANUFACTURING POROUS FILM

(57) Abstract:

PROBLEM TO BE SOLVED: To provide a method and apparatus for continuously manufacturing a porous polymer film industrially, capable of homogenously controlling porous characteristics such as film thickness, a pore size, voids, a pore shape or the like.

SOLUTION: A polymer solution with a solution viscosity of 10-30,000 poise is supplied on a belt conveyor to form a polymer solution cast film and, after the film thickness of this cast film is uniformly adjusted, a solvent substitution speed adjusting material is continuously supplied to be laminated on the polymer solution cast film. The laminate, which is constituted of the belt conveyor, the polymer solution cast film and the solvent substitution speed adjusting material, is immersed in a coagulation liquid comprising a non-solvent with respect to the polymer and moved through the coagulation liquid to precipitate the porous polymer film, and the laminate is immersed in a structure stabilizing solvent. While the laminate is immersed in the structure stabilizing solvent or after the laminate is taken out of the structure stabilizing solvent, the solvent substitution speed adjusting material and the porous polymer film are peeled from the laminate and the peeled porous polymer film is dried and/or heat-treated to continuously manufacture the porous film of which the porous characteristics such as film thickness, a pore size, voids, a pore shape or the like are homogenous.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] Adjusting a solvent permutation rate from the flow casting film of a polymer solution, this invention is the approach that polymer porous membrane can be obtained by the phase converting method, and relates to the manufacture approach of porous membrane and manufacturing installation which can obtain continuously the porous membrane in which especially variation has few penetrated homogeneous porous properties.

[0002]

[Description of the Prior Art] The porosity polymer film is broadly used for the material of industrial ingredients, such as a filter, a demarcation membrane, and a separator for cells, and a medical ingredient, the optical material, the electronic ingredient, etc. The manufacture approach of the porosity polymer film For example, the approach of carrying out extract removal of said non-subtlety granular powder object or the organic liquefied object, and forming pore, after mixing a non-subtlety granular powder object and an organic liquefied object to a polymer and producing a film to it, How to perform annealing treatment, form a lamellae laminated structure in a size enlargement object, and form pore by extending subsequently, making between this lamellae laminating crystal exfoliate, and growing up fibril, after carrying out size enlargement of the crystalline polymer, Moreover, a polymer solution is cast and there is the phase converting method make pore form using the phase separation phenomenon which is immersed in coagulation liquid (the solvent of a polymer solution has compatibility and a polymer is an insoluble organic solvent, water, etc.), and produces it in that case etc.

[0003] Said phase converting method is suitably used, when manufacturing porous membrane from polymers, such as cellulose acetate, polysulfone, a polycarbonate, polyvinyl alcohol, a polyamide, polyimide, and polyvinylidene fluoride. However, since the porous membrane obtained by the phase converting method was the asymmetric membrane by which the compact layer was formed in the outermost surface and pore was formed in the interior of the film, the application of the obtained film was limited to the gas separation membrane etc.

[0004] The manufacture approach of the polyimide porosity film which carries out the laminating of the porosity film to it after carrying out the cast of the polyamic acid solution to JP,11-310658,A, and is characterized by immersing this layered product in a poor solvent is indicated. According to this approach, the polyimide porous membrane which has a through tube with a diameter of about 0.01-10 micrometers was able to be obtained. The porous membrane which has the penetrated micropore which is obtained by this approach is very useful in the aforementioned various applications.

[0005]

[Problem(s) to be Solved by the Invention] This invention is offering the continuation manufacture approach and continuation manufacturing installation of industrial porous membrane which can control porosity properties, such as thickness, an aperture, a void content, and a hole configuration, to homogeneity in the approach of obtaining the porous membrane shown in said JP,11-310658,A.

[0006]

[Means for Solving the Problem] The process which this invention supplies the polymer solution whose solution viscosity is 10-30000poise on a band conveyor for the purpose of solving an above-mentioned technical problem, and forms the polymer solution flow casting film, The process which adjusts said polymer solution flow casting film to uniform thickness, and the process which supplies solvent permutation speed-regulation material continuously, and is stuck on said polymer solution flow casting film, The process which it is immersed [process] into the coagulation liquid containing a non-solvent [as opposed to said polymer for the layered product which consists of the band conveyor and polymer solution flow casting film which were formed at said process, and solvent permutation speed-

regulation material], and moves the inside of coagulation liquid, and deposits the porosity polymer film, The process which exfoliates solvent permutation speed-regulation material and the porosity polymer film from said layered product in Ushiro who took out said layered product under immersion or from said structure stabilization solvent the process immersed into a structure stabilization solvent, and in said structure stabilization solvent, It is related with the continuation manufacture approach of the porous membrane constituted including desiccation and/, or the process to heat-treat in said exfoliative porosity polymer film. Furthermore, the band conveyor which can drive this invention and the feed zone which supplies a polymer solution, The thickness controller of the polymer solution flow casting film, and the feed zone and the lamination section which supply solvent permutation speed-regulation material continuously, and are stuck on said polymer flow casting film, It is constituted including a coagulation cistern and a structure stabilization solvent tub, and the exfoliation section of solvent permutation speed-regulation material and the porosity polymer film. Stick solvent permutation speed-regulation material on said flow casting film by Ushiro in which the polymer solution flow casting film of homogeneous thickness was formed on the band conveyor, and a layered product is formed. Subsequently, said layered product is immersed in coagulation liquid, and the inside of coagulation liquid is moved, and it is related with the continuation manufacturing installation of the porous membrane constituted so that the porosity polymer film might be deposited.

[0007]

[Embodiment of the Invention] The continuation manufacture approach of porous membrane given in this application claims 1-6 and a continuation manufacturing installation given in this application claims 7-10 have the relation corresponding to mutual so that each configuration of each may state below.

[0008] The continuation manufacturing method of the porous membrane of this invention is explained. A polymer is dissolved in homogeneity into a solvent and degassing of the polymer solution is carried out enough. The polymer concentration of said polymer solution is 1 - 30 % of the weight preferably 0.3 to 60% of the weight. At less than 0.3 % of the weight, since control of a deposit of a polymer will become difficult if 60 % of the weight is exceeded preferably, since the reinforcement of the porous membrane obtained falls, it is not desirable. Moreover, 10-30000poise (rotation viscosity) of 50-10000poise of solution viscosity of a polymer solution is 100-5000poise especially preferably preferably. Since it will be made to cast easily on a band conveyor or it will become difficult it to become difficult to adjust thickness to homogeneity, and for control of a solvent permutation rate to become difficult, and to control porosity properties, such as an aperture, a void content, and a hole configuration, to homogeneity if solution viscosity exceeds 30000poise, it is not suitable. Since it becomes impossible to hold the configuration as flow casting film in less than 10poise, and it is easy to produce thickness nonuniformity and it has become, it is not suitable. In order to obtain uniform thickness, it is suitable for said polymer solution to be supplied on a band conveyor with constant flow. Since the approach of extruding a polymer solution from a nozzle (T die) by pressurizing the inside of the feeder which stored the polymer solution as the supply approach at a fixed pressure using a gas especially dry air, or inert gas can prevent mixing of air bubbles etc., it is desirable. As for a polymer solution, it is desirable to be supplied by the T die with constant flow with fixed width of face on a band conveyor.

[0009] As for a band conveyor, what has the detachability which can remove easily the porous membrane in which a front face is smooth and deposited-is desirable. Moreover, since endurance needs to be excellent even if it contacts an organic solvent, a metal belt, especially the belt made from stainless steel are desirable. Moreover, a band conveyor is what can change a rate, and that from which fluctuation becomes whenever [constant-speed] few is suitable for it during a drive.

[0010] As for the polymer solution flow casting film cast on the band conveyor, thickness is adjusted. Although it is suitably performed by the blade (doctor knife) which is installed so that it may have a uniform clearance a band conveyor and crosswise, and can adjust the clearance, since adjustment of thickness needs to adjust thickness with a sufficient precision to homogeneity, it is desirable to be carried out by the part which the belt inferior surface of tongue supports with the roll or the plate. Moreover, in the approach of this invention, 1-2000 micrometers of polymer flow casting thickness are especially adjusted to 10-500 micrometers preferably. The reinforcement of the porous membrane which will be obtained if thickness is smaller than 1 micrometer becomes less enough, and is not desirable. Moreover, since it becomes difficult to control porosity properties, such as an aperture, a void content, and a hole configuration, to homogeneity since the homogeneity of the vesicular structure of the direction of thickness of the porous membrane which will be obtained if thickness exceeds 2000 micrometers worsens, it is not desirable.

[0011] Subsequently, solvent permutation speed-regulation material is stuck on said polymer solution flow casting film. It is suitable in the case of this lamination that a pressure is controlled so that the thickness of the polymer solution flow casting film does not change substantially. Not changing substantially are 90% or more of thickness, and sticking it preferably, as 95% or more of thickness's is held to the thickness of Saki's polymer flow casting film

stuck. Since it will become difficult for a polymer solution to flow compulsorily, and for the variation in flow casting thickness to become large, and to control porosity properties, such as thickness of the porous membrane obtained, an aperture, a void content, and a hole configuration, to homogeneity if the pressure when sticking is high, it is not desirable.

[0012] Moreover, although the lamination of said solvent permutation speed-regulation material moves the polymer solution flow casting film on a band conveyor to an abbreviation horizontal direction and it does not matter that it is ***** the polymer solution flow casting film on a band conveyor -- an abbreviation perpendicular direction -- or, moving the polymer solution flow casting film below to a perpendicular direction at the include angle of 60 or less (from an abbreviation perpendicular to 45 or less degrees [Preferably]) degrees by the condition of having turned up Especially since thickness of the polymer flow casting film cannot change easily due to the weight of the solvent permutation speed-regulation material which sticking solvent permutation speed-regulation material on said polymer solution flow casting film stuck, it is suitable. For example, especially the thing for which lamination is performed is suitable while progressing, while the layered product of a band conveyor and the polymer flow casting film changes a direction from an abbreviation horizontal direction to an abbreviation perpendicular direction with a roll.

[0013] The solvent permutation speed-regulation material of this invention is a porosity film, and in case it contacts the polymer flow casting film in coagulation liquid and deposits a polymer, what has the permeability which is extent which the solvent and coagulation liquid of a polymer solution can penetrate at a suitable rate is desirable. Especially, that whose air permeability (gar rhe value) is 50 - 1000 seconds / 100 cc, and further 250 - 800 seconds / 100 cc is desirable. The thickness of solvent permutation speed-regulation material is 5-100 micrometers, and 5-500 micrometers of things which the aperture penetrated in the direction of a film cross section is distributing by 0.01-10 micrometers and desirable consistency with a 0.03-1-micrometer sufficient hole are preferably suitable for it. Since it becomes impossible to adjust enough a solvent permutation rate -- a compact layer is formed in the polymer front face which a solvent permutation rate is too quick and deposits -- when the air permeability of solvent permutation speed-regulation material is larger than the above-mentioned range, if it is not suitable and is smaller than the above-mentioned range, a solvent permutation rate will become slow too much, and the vesicular structure formed in a deposit polymer will become an ununiformity.

[0014] Since it excels in the smooth nature on the front face of a film of the manufactured porous membrane when a nonwoven fabric or porous membrane made from polyolefines, such as polyethylene and polypropylene, a cellulose, Teflon (trademark), etc. is specifically used as solvent permutation speed-regulation material and the fine porosity film made from polyolefine is used especially, it is suitable.

[0015] In this invention, the layered product on which a band conveyor, the polymer flow casting film, and solvent permutation speed-regulation material were stuck is immersed in coagulation liquid, and the inside of coagulation liquid is moved, and the porosity polymer film is deposited. In coagulation liquid, a non-solvent contacts the polymer solution flow casting film through solvent permutation speed-regulation material, and is gradually permuted by the solvent in the polymer solution flow casting film, and the ***** porosity polymer film deposits [the phase separation of the polymer solution flow casting film]. If the permutation of this solvent and a non-solvent inclines and it is carried out that there is nothing, porosity properties, such as thickness of the porous membrane obtained, an aperture, a void content, and a hole configuration, can be made into homogeneity. The thickness of the porous membrane obtained since the progress condition of phase separation will not become homogeneity, if variation arises in the permutation of a solvent and a non-solvent, an aperture, a void content, a hole configuration, etc. become heterogeneity. One of the descriptions of this invention moves said layered product in coagulation liquid, and it is to deposit the porosity polymer film, making the solvent which touches said layered product front face always refresh. That is, porosity properties, such as thickness of the porous membrane obtained, an aperture, a void content, and a hole configuration, are controlled more to homogeneity by controlling by always refreshing the solvent which touches a front face in the local concentration of a solvent and a non-solvent which happens when the solvent in the polymer flow casting film and the non-solvent in coagulation liquid permute, and the bias of a presentation, inclining and advancing the permutation of a solvent and a non-solvent that there is nothing.

[0016] Moreover, in this invention, the rate, i.e., the rate of a band conveyor, which makes the layered product on which a band conveyor, the polymer flow casting film, and solvent permutation speed-regulation material were stuck advance into coagulation liquid has desirable 0.01m 50m part for / - and thing [a part for /]. By 0.01m/, in the following, since productivity is bad, it is not suitable, and if a part for 50m/is exceeded, since equipment becomes large too much and a problem arises in control of belt driving, management of coagulation liquid (coagulation tub), etc., it is not desirable.

[0017] As coagulation liquid of this invention, the non-solvent of said polymer or a 99.9 - 40 % of the weight of non-

[these] solvents and 0.1 - 60 % of the weight [of solvents of said polymer solution] mixed solvent can be used. Since the structure of the porous membrane which deposits tends to become homogeneity when the mixed solvent which becomes coagulation liquid from a non-solvent and a solvent is used, it is suitable. That is, the non-solvent used as coagulation liquid is a polymer non-solvent, and has the solvent and compatibility of a polymer solution, and ether, such as ketones, such as alcohols, such as a methanol, ethanol, and isopropyl alcohol, and an acetone, and diethylether, water, etc. are used.

[0018] Subsequently, a band conveyor, the porous membrane which deposited, and solvent permutation speed-regulation material are in the stuck condition, and it is immersed into a structure stabilization solvent. A structure stabilization solvent removes completely the solvent of the polymer solution which remains in the porous membrane which deposited in said coagulation liquid, and stabilizes a vesicular structure. Although said coagulation liquid may have the operation to which the phase separation of a polymer solution is urged and the mixed liquor of a non-solvent and a solvent etc. may be used, a structure stabilization solvent has the solvent desirable [compatibility] in which solubility is not shown to a polymer, although it has coagulation liquid and compatibility. For example, lower alcohol, a hexane, water, etc. can be used suitably.

[0019] Furthermore, the structure stabilization solvent also has the effectiveness which promotes exfoliation with a band conveyor, the porous membrane which deposited, and solvent permutation speed-regulation material. Therefore, while being immersed into the structure stabilization solvent, solvent permutation speed-regulation material and the porous membrane which deposited may be made to exfoliate. Or after taking out out of a structure stabilization solvent, solvent permutation speed-regulation material and the porous membrane which deposited may be made to exfoliate. It is not desirable in order for a vesicular structure to acquire a lifting and the uniform porosity property which becomes empty for deformation, since stress and heat can be applied into porous membrane after the solvent of a polymer solution has remained considerably if solvent permutation speed-regulation material and porous membrane are made to exfoliate without being immersed in a structure stabilization solvent, and desiccation and heat treatment are performed.

[0020] the porous membrane which exfoliated from solvent permutation speed-regulation material and a band conveyor -- subsequently -- desiccation and/or or it heat-treats. As for this process, it is desirable to process suitably according to the class of polymer or the class of used solvent, respectively. For example, finally in the porous membrane of polyamic acid, polyimide porous membrane can be obtained by performing and forming elevated-temperature heat treatment in a 200 degrees C - 500 degrees C temperature requirement into heat imide following 80-100-degree C hot air drying. Since the porous membrane which was made to stabilize vesicular structures (hole a configuration, an aperture, etc.), and had uniform porosity can be obtained, it is suitable to carry out to the film by applying fixed tension with a tension roll, in order to support crosswise both ends by a pin tenter etc. in the case of these desiccation and heat treatments in order to control the heat shrink of the cross direction of porous membrane, to apply fixed tension and to control the heat shrink of the lengthwise direction of this film.

[0021] That what is necessary is just the polymer used in the usual phase converting method, although cellulose acetate, polysulfone, a polycarbonate, polyvinyl alcohol, a polyamide, polyimide, polyvinylidene fluorides, those precursors, those mixture, etc. can be used suitably, since it has the property which was extremely excellent in thermal resistance, a solvent-proof, **** stability, insulation, etc., the polymer used in this invention can be used that aromatic polyimide or an aromatic polyimide precursor is especially useful and suitably.

[0022] The case where a polyimide precursor is used as a polymer below is explained. Said polyimide precursor is a tetracarboxylic acid component, a diamine component, the polyamic acid obtained by carrying out the polymerization of the aromatic series monomer preferably, or its thing which can imide-ize partially and can carry out a ring closure by heat imide-ization or forming chemistry imide and which can be used as polyimide resin. The rate of imide-izing of polyimide resin is about 95% or more of heat-resistant polymer suitably about 80% or more.

[0023] As for the organic solvent used as a solvent of said polyimide precursor, the parachlorohenol, a N-methyl-2-pyrrolidone (NMP), a pyridine, N,N-dimethylacetamide, N,N-dimethylformamide, dimethyl sulfoxide, tetramethylurea, a phenol, cresol, etc. are mentioned.

[0024] an aforementioned tetracarboxylic acid component and an aforementioned aromatic series diamine component -- the inside of the above-mentioned organic solvent -- the profile equimolar dissolution -- carrying out -- a polymerization -- carrying out -- a logarithm -- the polyimide precursor whose viscosity (30 degrees C, concentration; 0.5g/100mL NMP) is especially 0.5-7 0.3 or more is manufactured. Moreover, when a polymerization is performed at the temperature of about 80 degrees C or more, the polyimide precursor which carried out [the precursor] the ring closure partially and was imide-ized is manufactured.

[0025] As the aforementioned aromatic series diamine, it is a general formula (1), for example.

H₂N-R(R₁)m-A-(R₂)nR'-NH₂ (1)

(-- however, in said general formula, R and R' is direct coupling or the aromatic series ring of bivalence, R₁ and R₂ are substituents, such as a hydrogen, low-grade alkyl, and low-grade alkoxy ** halogen atom, A is the radical of bivalence, such as direct coupling, or O, S, CO, SO₂, SO, CH₂, C(CH₃)₂, and m and n are the integers of 1-4.) -- the aromatic series diamine compound shown is desirable.

[0026] as the concrete compound of said aromatic series diamine - diamino diphenyl ether (it may be hereafter written as DADE), and 4 and 4 '3, 3'-dimethyl - 4 and 4 - diamino diphenyl ether, and '3, 3' - diethoxy -4 and 4' - diamino diphenyl ether, a p phenylenediamine, etc. are mentioned.

[0027] Moreover, as the aforementioned aromatic series diamine component, you may be a diamino pyridine and, specifically, 2, 6-diamino pyridine, 3, 6-diamino pyridine, 2, 5-diamino pyridine, 3, and 4-diamino pyridine etc. is mentioned. Two or more sorts of aromatic series diamine components may be used combining each above-mentioned aromatic series diamine component.

[0028] As the aforementioned tetracarboxylic acid component, a biphenyl tetracarboxylic acid component is mentioned suitably. For example, 3, 3', 4, 4'-biphenyl tetracarboxylic dianhydride Although (it may be hereafter written as s-BPDA), 2 and 3, 3', and 4-biphenyl tetracarboxylic dianhydride are desirable 3, 3', and 4 and 4 - or '2, 3, 3', and 4 -- you may be the salts or those ester derivatives of - biphenyl tetracarboxylic acid or '3, 3', 4, and 4' - or 2 and 3, 3', 4'-biphenyl tetracarboxylic acid. A biphenyl tetracarboxylic acid component may be the mixture of each above-mentioned biphenyl tetracarboxylic acid.

[0029] Moreover, the above-mentioned tetracarboxylic acid components may be tetracarboxylic acid, such as a pyromellitic acid, 3, 3', 4, 4'-benzophenone tetracarboxylic acid, 2, and 2-bis(3, 4-dicarboxy phenyl) propane, a bis(3, 4-dicarboxy phenyl) sulfone, the bis(3, 4-dicarboxy phenyl) ether, bis(3, 4-dicarboxy phenyl) thioethers or those acid anhydrides, a salt, or an esterification derivative. Moreover, a part of these aromatic series tetracarboxylic acid component may be replaced to all tetracarboxylic acid components at a 10 mol % less or equal, especially a rate not more than 5 mol % by aliphatic series tetracarboxylic acid, such as butane tetracarboxylic acid or those acid anhydrides, a salt, or an esterification derivative.

[0030] The aforementioned polyimide precursor dissolves in said organic solvent at 1 - 30% of the weight of a rate preferably 0.3 to 60% of the weight, and is prepared by the polyimide precursor solution (an organic solvent may be added or a polymerization solution may be used as it is). Since the film reinforcement at the time of producing porous membrane will fall if the rate of a polyimide precursor is smaller than 0.3 % of the weight, it is not suitable, and since solution viscosity will become [solution viscosity control] difficult highly, flow casting will become difficult, and control of a porous membrane deposit will become difficult, if larger than 60 % of the weight, and it is not desirable, the above-mentioned range is suitable. in the aforementioned polymer concentration, a polymer solution is suitable solution viscosity -- 50-10000poise 10-30000poise can be adjusted especially easily [it is desirable and] for 100-5000poise more preferably.

[0031] Porous membrane which consists of a polyimide precursor obtained in this invention method is formed into heat imide by heat-treatment, and is used as polyimide porous membrane. Although chemistry imide-ization can also carry out [imide]-izing, since there is an inclination for the reinforcement of the film obtained to become large in addition to a process not becoming complicated by the approach of forming into heat imide, it is suitable. Heat imidization can be suitably performed by heat-treating for [for / 5 minutes / -] 60 minutes at 250 degrees C - 500 degrees C in atmospheric air as above-mentioned.

[0032] Next, drawing 1 which is the schematic diagram of a typical operation gestalt - drawing 4 explain the continuation manufacturing installation of the porous membrane of this invention. In addition, the continuation manufacturing installation of this invention is not limited to the operation gestalt shown in the schematic diagram of drawing 1 - drawing 4. The continuation manufacturing installation of this invention is equipped with the band conveyor 1 which is rate adjustable and is driven by constant speed. As for a band conveyor 1, what has the detachability which can remove easily the porous membrane in which a front face is smooth and deposited is desirable. Moreover, since endurance needs to be excellent even if it contacts an organic solvent, a metal belt, especially the belt made from stainless steel are desirable.

[0033] Moreover, it has the feed zone 2 which supplies a polymer solution with constant flow. This feed zone holds a polymer solution, where degassing is carried out, is constant flow and supplies it on a band conveyor from a nozzle (or T die) 3. the sealed container which contained the polymer solution although supply could be performed using the pump -- a gas -- it can carry out suitably by the approach of pouring in inert gas, such as dry air or nitrogen gas, preferably, and extruding a polymer solution with constant flow with a fixed pressure, without making air bubbles mix. Moreover, although the supply gestalt to a band-conveyor top has the approach of extruding from a nozzle, the

approach of carrying out a spray, etc. and those nozzles traverse crosswise [of a belt], what is supplied crosswise to homogeneity with constant width through the T die which has a slit crosswise [of a belt] is suitable. If it carries out like this, even when solution viscosity is comparatively high, the flow casting film of the polymer solution to which thickness was equal can be formed. The formed flow casting film moves with a belt, and has thickness adjusted by the thickness controller 4 in a higher precision. The thickness controller 4 is constituted by the blade (doctor knife) which placed the fixed clearance and it had to the belt front face. The magnitude of a clearance is adjustable. Moreover, in order to support by the plinth in which a belt inferior surface of tongue has a roll and a smooth front face in order to adjust thickness with a sufficient precision to homogeneity or to prevent the play of a belt further, it may be constituted so that an inferior surface of tongue may be attracted and a smooth side may be adsorbed.

[0034] Moreover, the continuation manufacturing installation of this invention is equipped with the feed zone 5 and the lamination section 6 of solvent permutation speed-regulation material. For example, solvent permutation speed-regulation material is continuously supplied from a supply roll, and the feed zone 5 of solvent permutation speed-regulation material is stuck in the lamination section 6 on the polymer solution flow casting film which was guided by the pinch roll and formed on the band conveyor. Under the present circumstances, the clearance between a pinch roll and a band conveyor can be adjusted so that the pressure of extent from which the thickness of the polymer flow casting film does not change substantially even if solvent permutation speed-regulation material is stuck may be applied. moreover, the lamination section, although the polymer solution flow casting film on a band conveyor is moved to an abbreviation horizontal direction and it may be constituted by obtaining ***** the polymer solution flow casting film on a band conveyor -- an abbreviation perpendicular direction -- or, moving the polymer solution flow casting film below to a perpendicular direction at the include angle of 60 or less (preferably 45 or less degrees) degrees by the condition of having turned up If it is constituted so that solvent permutation speed-regulation material may be stuck on said polymer solution flow casting film, especially since thickness of the polymer flow casting film cannot change easily due to the weight of the stuck solvent permutation speed-regulation material, it is suitable. For example, if it is constituted so that lamination may be performed by the part by which a band conveyor and the polymer flow casting film are led to a roll, and go to the abbreviation perpendicular direction from the abbreviation horizontal direction as shown in drawing 1 - drawing 4, since fluctuation of thickness etc. cannot take place [the polymer solution flow casting film] easily in response to effect due to the weight of solvent permutation speed-regulation material, it is suitable.

[0035] Moreover, it is desirable to be constituted so that the humidity and temperature of the space through which the band conveyor 1 from the polymer solution feed zone 2, the thickness controller 4 of the flow casting film, the lamination section 6 of solvent permutation speed-regulation material, and the lamination section to the coagulation cistern 7 passes can be controlled by the continuation manufacturing installation of this invention. Since temperature affects polymer solution viscosity, it is necessary to control it uniformly. Moreover, if it does not hold to low humidity when the hygroscopic solvent is used, a solvent will absorb moisture moisture and the problem of becoming it being easy to deposit a polymer will arise. Since temperature and humidity affect a phase separation deposit process, when managing uniformly controls porosity properties, such as an aperture, a void content, and a hole configuration, to homogeneity, they are important. Furthermore, in order to avoid the effect of dust, as for the air cleanliness class of such space, it is desirable to have clean-sized equipment so that it may be held at required level.

[0036] Moreover, the continuation manufacturing installation of this invention is equipped with the coagulation cistern 7 and the structure stabilization solvent tub 8. Above-mentioned coagulation liquid and an above-mentioned structure stabilizer are stored in these tubs, respectively. It consists of this inventions so that it may be immersed in coagulation liquid and the layered product which stuck a band conveyor, the flow casting film of a polymer solution, and solvent permutation rate accommodation material may move in the inside of coagulation liquid. The solvent and coagulation liquid solvent of a polymer solution permute gradually during immersion, phase separation is started, and porous membrane deposits. It is very important when permuting these solvents by homogeneity controls porosity properties, such as an aperture of porous membrane, a void content, and a hole configuration, to homogeneity. The solvent which is made to move said layered product in a coagulation liquid solvent, and touches a layered product front face is made to always refresh, and it consists of this inventions so that the bias of local solvent concentration may be controlled. Moreover, since immersion needs to be performed enough, you may have two or more these tubs. Moreover, like the operation gestalt of drawing 2, as a layered product moves in a zigzag direction within a coagulation cistern, it may be constituted so that sufficient immersion time amount may be earned. Since phase separation is influenced with the presentation of temperature or a solvent, it is suitable for a coagulation cistern that management of temperature, a solvent presentation, etc. is performed enough.

[0037] Moreover, in the manufacturing installation of this invention, you may be constituted so that said layered

product may make it advance into an abbreviation perpendicular to coagulation liquid like drawing 1 and the operation gestalt of drawing 2, and it does not matter even if it is constituted so that said layered product may incline to a coagulation liquid front face like drawing 3 and the operation gestalt of drawing 4 and it may advance into coagulation liquid. Moreover, it constitutes so that a layered product may incline and move to a coagulation liquid front face like the operation gestalt of drawing 4 at the process which said layered product advances and moves to coagulation liquid. Moreover, if it constitutes so that a layered product may incline and move to a coagulation liquid front face also at the process taken out from coagulation liquid Since adjustment of making water level of coagulation liquid high, lengthening immersion time amount (immersion distance), or making water level of coagulation liquid low and shortening immersion time amount (immersion distance) can be performed easily, it is very suitable. Furthermore, since the threshold speed to the coagulation liquid of a layered product also affects it to a solvent permutation and phase separation deposit behavior, it is desirable for it to be able to adjust in 0.01m a part for /-, and 50m range for /.

[0038] Moreover, in the manufacturing installation of this invention, although especially the drive of a band conveyor is not limited and can use the usual drive approach, it is suitably performed using a drive roll or a free roll. Moreover, with a roll as shown by 13 of drawing 1 - drawing 4, since the solvent permutation speed-regulation material of a layered product contacts a roll surface and directly, in order to ease the compressive stress which joins porous membrane, what covered the roll surface with elastic bodies, such as rubber, is used suitably. Since a porous gestalt may deform porous membrane in response to compressive stress with metals, such as stainless steel, the front face of such a roll is not desirable.

[0039] The exfoliation section 9 of solvent permutation rate accommodation material and the exfoliation section 10 of porous membrane which deposited may be incorporated so that the structure stabilization solvent tub 8 may exfoliate solvent permutation rate accommodation material and/, or the porous membrane that deposited in a structure stabilization solvent. In this case, since each exfoliation becomes easy, it is suitable to arrange so that porous membrane may be exfoliated in Ushiro who solvent permutation speed-regulation material was exfoliated [Ushiro] first, and contacted the solvent to porous membrane more. Moreover, the structure stabilization solvent tub 8, the exfoliation section 9 of solvent permutation rate accommodation material, and the exfoliation section 10 of porous membrane may be constituted so that solvent permutation rate accommodation material and/, or the porous membrane that deposited may be exfoliated in Ushiro who came out of the structure stabilization solvent.

[0040] As for the porous membrane which exfoliated, desiccation and/, or heat treatment is performed. For that, it has an air forced oven and/, or an elevated-temperature thermal treatment equipment. the porous membrane which united an air forced oven and/, or an elevated-temperature thermal treatment equipment with a polymer feed zone to the exfoliation section, and exfoliated -- continuous -- desiccation and/-- or you may be constituted so that it may heat-treat, or an air forced oven and/, or an elevated-temperature thermal treatment equipment may be arranged so that it may become another process about desiccation and/, or heat treatment.

[0041] Porous membrane with the vesicular structure which has especially the detailed continuation hole whose void content is 15 - 85%, and whose average aperture is 0.01-10 micrometers preferably by this invention can be obtained. This detailed continuation hole leads in nonlinear, while pore is following the shape of a path to other front faces and is crooked from the front face of arbitration. Moreover, even if a void content makes it high, its mechanical strength is high, and since the porous membrane obtained by this invention is moreover porous membrane with homogeneous porosity properties, such as thickness, an aperture, a void content, and a hole configuration, it is very useful in various applications.

[0042] [Example] Next, an example explains this invention. However, this invention is not limited to the following examples.

(Example of reference)

s-BPDA was used as an adjustment tetracarboxylic acid component of a polyamic acid solution, DADE was used as a diamine component, the mole ratio of DADE to S-BPDA is 0.996, and it dissolved in NMP so that the sum total weight of this monomer component might become 10% of the weight, and the temperature of 40 degrees C and a 6-hour polymerization were performed, and the polyimide precursor solution was obtained. The solution viscosity of a polyimide precursor solution was 800poise.

[0043] (Example)

Porous membrane was manufactured using the equipment in which the schematic diagram was shown by manufacture drawing 4 of porous membrane. After obtaining to a polymer feed zone in the example of reference, it cast into it on the band conveyor of the product made from stainless steel which pours in the nitrogen gas which poured in the

polyimide precursor solution which carried out reduced pressure deaeration so that air bubbles might not be involved in, and pressurized it at 2.5kg/cm², and drives said polyimide precursor solution with 0.3m speed for /through a T die with the pressure, and the thickness controller adjusted the thickness of the flow casting film to 100 micrometers continuously. Using polyethylene porous membrane (Ube Industries, Ltd. make, you pore UP2015, and air permeability 550 seconds /, 100 cc) as solvent permutation speed-regulation material, through the pinch roll, on said flow casting film, substantially, as thickness did not change, it was stuck. These processes were performed under the ambient atmosphere of the temperature of 23 degrees C, and 50% of relative humidity. Next, the layered product which stuck a band conveyor, the flow casting film, and polyethylene porous membrane was made to advance into the coagulation cistern in which the methanol was stored, the inside of coagulation liquid was moved for 5 minutes, it was immersed, and polyimide precursor porous membrane was deposited. After having led this to the structure stabilization solvent tub in which water was stored from the coagulation cistern with a roll further, being immersed and coming out of a structure stabilization solvent tub, it exfoliated, solvent permutation speed-regulation material was removed, and, subsequently polyimide precursor porous membrane was exfoliated from the band conveyor.

[0044] Next, both ends were fixed by the pin located in a line at sufficient spacing to support the film, and crosswise contraction was controlled, and applying the tension of extent which controls contraction to a travelling direction, the desiccation tub with a temperature of 80 degrees C was passed in 10 minutes, and it dried, and polyimide precursor porous membrane passed the 400-degree C heat treatment tub in 20 minutes continuously, performed heat imidization, and obtained polyimide porous membrane.

[0045] The obtained polyimide porous membrane had flexibility and had 30.0-micrometer uniform thickness, and when the methanol was dropped at the front face, it had the continuation hole penetrated at the rear face. When observed with the scanning electron microscope, the average aperture was high porous membrane with a homogeneity of 0.23 micrometers, and air permeability of the void content was 160 seconds / 100 cc at 65%.

[0046] Furthermore, the result of having sampled the polyimide porous membrane which carried out continuation manufacture exceedingly every 10m, and having measured an average aperture and air permeability is shown in Table 1. The average was [standard deviation of the aperture] 0.022 in 0.24 micrometers, and the average was [standard deviation of air permeability] 11.0 in 155 seconds / 100 cc. Moreover, as for thickness, the average of standard deviation was 1.004 in 29.9 micrometers.

[0047]

[Table 1]

サンプルNo.	平均孔径 (μ m)	透気度 (秒 / 100cc)	膜厚(μ m)
1	0.23	160	30.0
2	0.20	165	29.0
3	0.28	143	29.0
4	0.24	155	31.0
5	0.27	140	29.0
6	0.24	166	30.0
7	0.26	135	31.0
8	0.23	146	29.0
9	0.25	156	28.5
10	0.22	164	29.0
11	0.21	170	31.0
12	0.26	146	32.0
13	0.22	165	30.0
14	0.25	151	30.0
15	0.24	164	30.0
合計値	3.60	2326	448.5
平均値	0.24	155	29.9
標準偏差	0.022	11.0	1.004
変動係数(%)	9.3	7.07	3.36

[0048] In addition, in this invention, the aperture of porous membrane and air permeability were measured by the following approach.

** the scanning electron microscope photograph of the average aperture film front face of porous membrane -- photographing -- opening of 50 or more points -- a hole -- area -- measuring -- this hole -- the degree type from the

average of area -- following -- a hole -- it asked for the average diameter at the time of presupposing that a configuration is a perfect circle from count. Sa of a degree type means the average of hole area.

Average aperture = $2x(Sa/\pi) 1 / 2^{**}$ air permeability JIS It measured according to P8117. B mold gar rhe DENSO meter (Oriental energy machine company make) was used as a measuring device. The film of a sample is bound tight to the circular hole of 2 the diameter of 28.6mm, and an area of 645mm. With the container liner weight of 567g, the air in a cylinder is passed out of a cylinder from the trial circular hole section. The time amount which 100 cc of air passes was measured, and it considered as air permeability (gar rhe value).

** The thickness, area, and weight of the film cut off in void content predetermined magnitude were measured, and the void content was calculated by the degree type from eyes weight. The weight in which the film surface product measured S of a degree type, and thickness and w measured d, and D are polymer consistencies which form this porous membrane, for example, were set to 1.34 with aromatic polyimide.

Void content = $(1-W/(SxdxD)) \times 100[0049]$

[Effect of the Invention] Since this invention is what explained above, it does so effectiveness which is described below. By the continuation manufacture approach and continuation manufacturing installation of porous membrane of this invention, continuation manufacture of the porosity polymer film with homogeneous porosity properties, such as thickness, an aperture, a void content, and a hole configuration, can be carried out industrially.

[Translation done.]